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Analysis on air suspended particles of Coimbatore – a FTIR study

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Abstract : An infrared absorption method has been used to identify the minerals in dust collected from some parts of Coimbatore, Coimbatore district, Tamil Nadu without grinding. The KBr pellet technique was employed. The results obtained from the IR spectra show the presence of quartz, asbestos, kaolinite, calcite, haematite, montmorllonite, nacrite and coal. The hazardous effect of inhalation of these minerals are explained. The results show Pollachi main road is more contaminated with hazardous minerals.

Keywords : FTIR, air suspended particles – mineral

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1. Introduction

The atmosphere is a dynamic system, which steadily absorbs various pollutants from natural as well as man-made sources, thus acting as a natural sink. Gases such as CO, CO_2, H_2S, SO_2 and NO_2 as well as particulate matter such as sand and dust, are continually released into the atmosphere through natural activities such as forest fires, volcanic eruptions, decay of vegetation, winds and sand or dust storms. Epidemiolgical and toxicological studies indicate a link between air pollution and respiratory conditions like bronchitis, bronchial asthma, pulmonary emphysema and lung cancer. Apart from these, dust or air suspended particles are playing an important role in health effects. Minerals are ubiquitous on the surface of the earth. Naturally produced dust is a direct reflection of the average mineralogy of the earth's crust. Natural dust (airborne and/or suspended in water), therefore, is the result of weathering and erosion of several

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sources : unconsolidated sources, such as deserts and soil cover; and consolidated (lithic) sources, such as high mountain terrenes with non-vegetated areas and subarctic and arctic regions with essentially no growth cover and an absence of permanent ice. Organic dust originate from plants (or) animals while inorganic dusts can come from grinding metals (or) minerals such as rock (or) soil (silica, asbestos, coal, berilium, tin, barium and iron) [1]. Generally they are over 20μ in diameter although some are smaller. Most of the dust particles settle to the ground as dust fall, but particles 5μ (or) smaller tend to form stable suspension [2].

Several minerals are known to induce a variety of pulmonary diseases (pneumoconioses and Cancers) following inhalation. These mineral induced diseases include fibrosis, (a hardening of the lung associated with excess collagen), lung cancers, and mesothelioma (a rare cancer frequently associated with exposure to fibrous minerals). On the pathologies of diseases associated with exposure to mineral dusts and it became clear that a variety of minerals could affect the respiratory system. The identification of the mineralogical, geochemical and biochemical mechanisms are important in mineral induced pathogenesis requires an inter disciplinary approach, with bioscientists and geoscientists working together closely [3]. So the characterization of minerals in dust plays a vital role in research. The major dust source is soil and the components of such soil generated dust are various clay minerals and quartz. In the present investigation, dust samples collected from Coimbatore district of Tamilnadu are analysed using infrared spectroscopic technique.

2. Materials and methods

In the present investigation, the dust samples were collected from in and around area of Coimbatore, Tamil Nadu which are labeled as 1 to 12 (1-Mofussul Bus Stand, 2-Pollachi Main Road, 3-Town Bus Stand, 4-Ram Nagar, 5-Gandhipuram, 6-Seventh Street, 7-Coimbatore Junction, 8-Geetha Hall Road, 9-Town Hall, 10-Ukkadam, 11-Vadavalli, 12-Kalveerampalayam). Coimbatore area lies between latitude 11°25′ to 11°40' north and longitude 79°25′ to 79°40′ east in toposheet nos. 58M/6, M/7, M/10 and M/11. The dust (air suspended) particles which are deposited on tissue papers at the height of 20 feet in road side and land area are collected. These tissue papers are washed in distilled water. The settled dust particles at the bottom of container are then dried at 110°C in oven and are used for analysis.

Experimental technique : The major and minor minerals are qualitatively determined by using FTIR technique. The Nicolate avator 360 series is made use of in the present work for recording the FTIR spectra of the samples at room temperature. The samples are usually subjected to various pre-treatments in order to remove organic matter and certain other materials to improve the quality of the spectrum. Wet grinding is carried out by placing 5 to 10 mg of the sample in an agate mortar along with 10 to 15 drops of ethanol. The samples are ground most preferably by hand, avoiding vigorous rotatory motion until ethanol evaporates completely. Then the samples are mixed with KBr at various ratios 1:10, 1:20, 1:30, 1:40 and 1:50. The pellets were prepared and the spectra were taken. The maximum absorption and large number of peaks are observed for the samples in the ratio of 1:20 (sample-KBr) and chosen for analysis.

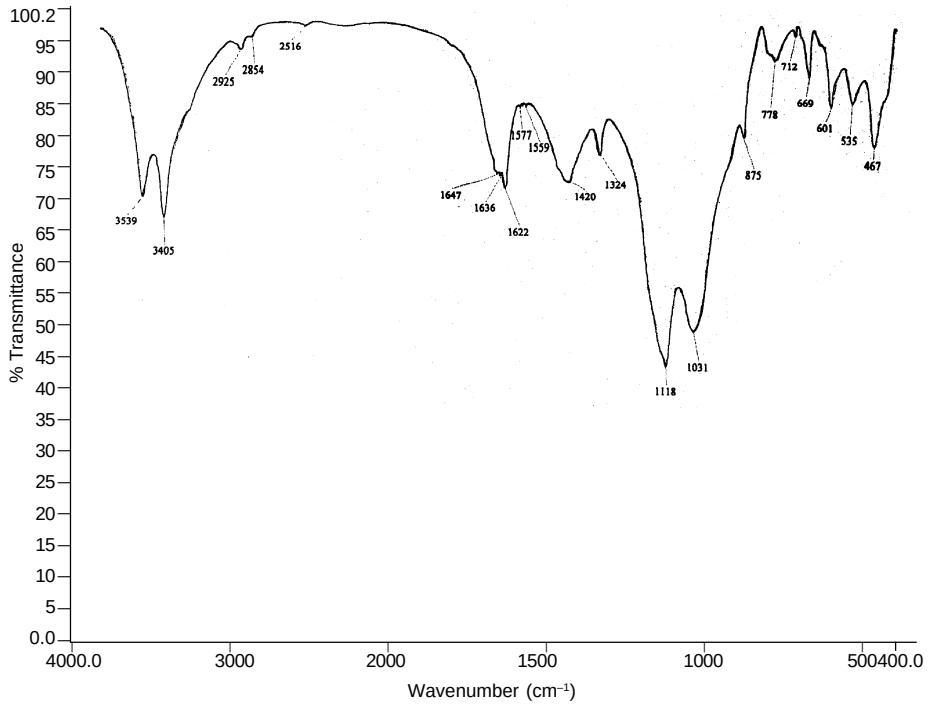

Figure 1. FTIR spectrum of the sample of site number 1.

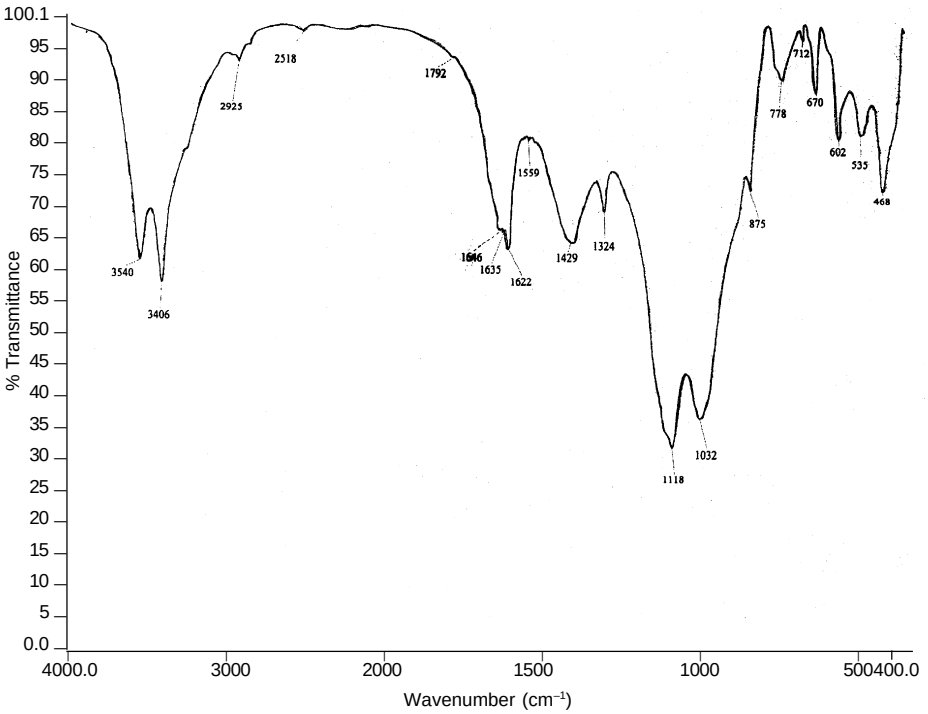

Figure 2. FTIR spectrum of the sample of site number 2.

From each area four samples were collected and from each sample three pellet specimens were prepared. The FTIR spectra are recorded in the region 4000 to 400cm^{-1}. One of the representative spectra of site numbers 1 and 12 are given in Figures 1 and 2.

3. Results and discussion

The FTIR spectra of all samples are analysed and the absorption frequencies of the peaks of various minerals (cm^{-1}) are reported in Table 1. From this Table, the absorption bands suggest the presence of quartz, asbestos, kaolinite, calcite, iron bearing mineral (haematite), montmorillonite and nacrite.

Table 1. Observed absorption frequencies (cm^{-1}) and its tentative assignment of bond vibrations of dust samples from the various sites of Coimbatore city given in mineral wise.

Mineral name	Observed frequency cm^{-1}	Site number	Mode of Assignment
Calcite	711–714	1,2,4 & 5	Doubly degenerate planar bending
	873–877	1,2,4,7 & 8	Out of plane bending
	1422–1425	1–12	Doubly degenerate planar bending
	1634–1638	1–4,6,9 & 11	
Quartz	464–468	1–12	Si–O Asymmetrical bending
	775–778	1–12	Si-O-Si Symmetrical stretching
Asbestos	1031–1034	1–12	Si-O Stretching
Kaolinite	1622–1626	1–12	Al-OH Vibration
	3689–3693	1–12	OH-Stretching of hydroxyl group
Hematite	532–534	1,8,11 & 12	Symmetrical bending
	584–588	1,8,11 & 12	
Montmorillonite	3404–3408	1–12	H-O-H Stretching of water molecule
Nacrite	3646–3648	1,8,10 & 12	Interlayer hydroxyl bonding
Coal	2920–2924	1–12	Carbon peak

Calcite

Among these minerals, calcite is present in all the samples. The frequency assignments reported by Hertzberg [4] for carbonate minerals are a symmetric stretching, ν_1; an out-of-plane bending, ν_2; a doubly degenerate asymmetric stretching, ν_3; and a doubly degenerate planer bending ν_4. But the symmetric oscillation represented by ν_1 is reported to be infrared inactive, hence only three fundamentals are ordinarily encountered. These have been recorded for various calcite group minerals in the regions of absorption at approximately 1430 cm^{-1} (ν_3), 909-833 cm^{-1} (ν_2) and 769-666 cm^{-1} (ν_4). In the present investigation, the spectra show the absorption bands at approximately 1424 cm^{-1} (all the samples), 875 cm^{-1} (sample number 1,2,4,7 and 8) and 712 cm^{-1} (sample number 1,2,4

and 5) and minor band at 1636 cm^{-1} (sample numbers 1,–4, 6,9 and 11) due to combinational modes of vibration. The absence of some peaks from sample to sample may be due to the interference of silicate minerals or due to the particle size of the minerals. If the particle size is minimum then the minerals are said to be disordered state.

Broadening of the absorption peak in the 1423–1476 cm^{-1} region include both the aragonite and calcite band positions appears also to be related to intergrowth of the two minerals. According to Adler and Kerr [5] when calcite mineral predominates in an aggregate, the peak appears in the range 1423 cm^{-1} and for aragonite in the range 1476 cm^{-1}. This statement supports the present investigation.

The symmetric stretching vibration, ν_3 lying between 1400–1450 cm^{-1} are particularly interesting, as these vibrations are particularly sensitive to the side symmetry for the carbonate group. In the view of William's [6] if the peak is in between this range, the mineral prevailing low pressure during the formation or this peak increases in splitting of this vibrational mode in calcite one can infer that the carbonate group becomes increasingly distorted in this phase with high compression. In the present case there is no splitting in this mode ν_3 but the peak at around 1423 cm^{-1} is present within the range 1400–1450 cm^{-1}. This indicates prevailing low pressure during the formation [7].

Quartz

The IR absorption frequencies observed for all the samples show the peaks in the range 464–471 and 777–780 cm^{-1}. The pattern of absorption in quartz can be explained by ascribing the 466 cm^{-1} region (Si-O asymmetrical bending vibrations), the bands in the region 780 (Si-O symmetrical stretching vibrations). This assignment is in good agreement with the observation on the quartz mineral obtained by many workers [8-14].

The characteristic feature of quartz is doublet centered at or around 780 cm^{-1} and 800 cm^{-1}. But in the present investigation, a peak at 777 cm^{-1} is alone present in almost all the samples with slight variation. The changes in this peak position may be due to the geological condition of formation like transport (or) deposition (or) by mechanical treatment such as grinding (or) weathering (or) pressure (or) temperature changes [15]. According to Jun Ojima [16], kaolinate and montmorillonite are the main interference minerals with quartz absorption. The present study shows these two minerals. Hence, the absence of the other characteristic peak of quartz such as 1096, 800, 695 and 514 cm^{-1} may be due to the interference of kaolinite and montmorillonite [16].

Crystallinity : The crystallinity is defined as the fraction of crystalline materials in a mixture of crystalline and non-crystalline material. It is otherwise called as degree of disorder. When crystallinity is minimum, the minerals are said to be in disordered state and maximum then the minerals are considered to be in ordered state.

Crystalline silica is one of the most abundant components in the dust samples both in natural and industrial environments. The crystalline nature of quartz may be confirmed

through the presence of peak at around 695 cm^{-1} [17]. But in the present investigation this peak is completely absent. According to Yariv and Mendelovici [18], the absorption of band at 695 cm^{-1} is due to the vibration of octa-hedral site symmetry and at 780 cm^{-1} is due to the vibration in the tetrahedral site symmetry. The tetrahedral symmetry is stronger one than octa-hedral site symmetry. The damage occurs first in octa-hedral then in terahedral symmetry if any structural change takes place. So the absence of 695 cm^{-1} may be due to the damage in the octahedral site symmetry of quartz in the dust samples. Hence, the present study indicates the presence of quartz is in disordered state which may be due to smaller particle size. According to Krivacsy and Hlavay [17], the inhalation of the disordered (or) crystalline silica can create the lung disease. The concentration of this quartz is proportional to the toxicity. Due to the presence of quartz in dust, the inhalation of the quartz particles in the size of 0.5 – 0.7 μm may produce diseases such as chronic silicosis, acute silicosis, accelerated silicosis and silica tuberculosis [19].

Asbestos

All asbestoses exhibit intense absorptions in the region 1200-900 cm^{-1} and 600-300 cm^{-1} of the infrared spectra. Most of the bands below 1200 cm^{-1} are attributed to Si-O streching and bending vibrations. On the lines of Coates [20] the presence of the band 609 cm^{-1} is due to chrysotile asbestos. However, this peak is completely absent in all site samples. This band is some what sensitive to interfere the other mineral silicates such as talc, kaolinite and montmorillonite which are present in almost all the samples. So this may be the reason for the absence of band at 609 cm^{-1} in all the samples. Due to the absence of this band at 609 cm^{-1} and the observation of other band 1033 cm^{-1} alone, confirms the presence of amphibole, other type of asbestos [20].

The presence of the "asbestos" in all the dust samples will create health hazards. The greatest hazard from asbestos is the inhalation of the fine dust fibrous and their retention in the lung and bronchial passages. This will create a thickening and scarring of lung tissue especially the inhalation of amphiboles will cause lung and bronchial cancers and mesothelioma. The particle size and shape play an important role in the inhalation and long penetration mechanisms, especially with amphibole fibrous [20].

Kaolinite

Kaolinite [$Al_2Si_2O_5$ $(OH)_4$], is one of the clay mineral which is extremely common in soils and in natural aerosols. The observed absorption frequencies in the regions 1624 cm^{-1} and 3690 cm^{-1} are the characteristic peaks of clay mineral kaolinite associated with dust samples. The obtained peak values of this mineral are very well matches with the results obtained by Russell [9], Small Wood and Hard [21], Ghosh [22], Ramaswamy and Venkatachalapathy [12] and Hlavay *et al* [8]. The intensity of the bands varies from sample to sample at different places. This means the amount of the kaolinite varies from sample to sample. The peak at 1624 cm^{-1} is due to H-O-H vibrations [23]. Kaolinite is a hydrothermally altered mineral in volcanic rock and a common component of coal mine dust. It is also one of the most common mineral in ceramic industry. Therefore, all the

samples in the present study are having kaolinite mineral [16]. The inhalation of this mineral in dust may develop a pneumoconiosis often referred to kaoliniosis. It is characterized by the presence of rounded opacities in the lung. This was done by Malcolm Ross *et al* [19].

Iron bearing minerals

Normally the dust samples have the iron bearing group of minerals such as maghemite ($MgFe_2O_3$), hematite (Fe_2O_3), magnetite (Fe_3O_4) and iron dust oxides. But according to the present results bared on IR technique, hematite mineral alone is present.

According to Russell [9] and Ramaswamy and Venkatachalapathy [12] the observed absorption frequencies present in all the samples show peaks in the range 528–539 cm^{-1}, 572-588 cm^{-1} and 640–645 cm^{-1} which are the characteristic peaks of hematite. The peak at around 534 cm^{-1} and 586 cm^{-1} are present only in the sample numbers 1,8,11 and 12. The peak at around 643 cm^{-1} is absent in all the samples. The reason for the absence of the peak at around 640 cm^{-1} may be due to the other interference minerals like quartz, kaolinite and asbestos (or) may be little amounts. The reason for the absence of other iron bearing minerals in the dust samples such as magnetite and maghemite may be due to the larger grain size. If the grain size is larger, then naturally it is not transported easily, because its specific gravity is much greater than that of other minerals. If the dust particle is in the range of 5 to 50 μm then, it will be easily transported through wind [25].

In all these samples, the intensities of the hematite peaks are weak to medium. Hence these mineral can be considered as trace mineral. thus the inhalation of such small grain sized iron bearing mineral (hematite) along with other minerals will also create lung disease, because the particles are coated in the surface of lungs.

Other minerals

From Table 1, the IR peaks are observed at 3406 cm^{-1} and 3648 cm^{-1} are due to OH-bending. The most distinguished feature of the montmorillonite is the broad absorption band ranges 3300–3500 cm^{-1} and 3540–3690 $cm^{"1}$ [10, 14]. The band in the range 3403–3407 cm^{-1} observed in this study sample may be due to H-O_H streching of water molecules present in the inter-layer region of montmorillonite $(Al, Mg)_2Si_4O_{10}(OH)_2.nH_2O$. This is a good agreement with the value 3406 $cm^{"1}$ reported by Maleolm and Summer [25].

Weismiller *et al* [26] reported the peaks at 3570 cm^{-1} and 3690 cm^{-1} for hydroxyl aluminium inter-layer material in montmorillonite OH-streching frequencies. But the peak at 3570 cm^{-1} is not observed in this study. If 3570 cm^{-1} peak is present it is non-pleochriotic. The absence of the peak 3570 cm^{-1} indicates the montmorillonite mineral is in disordered state. The peak at around 3648 cm^{-1} for the sample numbers 1, 8, 10 and 12 are observed, which is the characteristic peak of nacrite mineral [7]. The presence of this mineral shows the disorderedness of Kaolinite [27]. With reference to Mackenzie and

Rahman [28] kaolinite, nacrite and calcite are frequently co-exist in the clay fraction of soil and sediments. Hence, the presence of kaolinite (or) nacrite (or) calcite is unavoidable in dust samples. The absence of this peak in the sample numbers 2, 3, 4, 5, 6, 7, 9 and 11 may be due to the co-existence of kaolinite and nacrite. the peaks observed for both these minerals may overlap. Therefore, the inhalation of such small grain size minerals montmorillonite and nacrite along with other silicate and iron bearing minerals will create lung disease and cancer.

Coal is a combination of four groups such as aluminium silicates, carbonates,sulfides, silica. Aluminium silicates commonly found in coal are clay minerals such as kaolinite, montmorillonite, illite, mullite and muscovite. The confirmation of this coal dust is due to the presence of the peak at 2921 cm^{-1}. This peak indicates the reflectance of carbon content [29]. With the view of Thomason *et al* [29] if 3045 cm^{-1} peak is present in the sample then one can confirm presence of coal in the sample is plenty. But this peak is absent in all the present samples. This indicates the inclusion of coal, in all the samples are in trace amount. So the inhalation of these dust particle to cause pneumoconiosis disease. Pneumoconiosis is often referred to as black lung or anthraco silicosis is prevalent in coal miners [19].

3.1 Relative distribution of hazardous minerals :

The relative distribution of major minerals such as quartz, kaolinite, asbestos and calcite is explained through the determination of extinction co-efficient of the characteristic peaks of respective minerals.

The extinction co-efficient of above mentioned minerals have been calculated for all the air suspended samples under investigation, using the relation.

$$K = \frac{DA}{m}$$

where

K – Extinction co-efficient

D – Optical density (D = log I_0/I)

I_0 – Intensity of radiation before entering in the sample

I – Intensity of radiation after entering in the sample

A – Area of the pellet

m – Mass of the sample

The obtained values for quartz, kaolinite, asbestos and calcite are picturized in the Figure 3 to 6.

Quartz : The characteristic peak chosen for the determination of extinction co-efficient for the quartz is 777 cm^{-1}. From Figure 3, it is observed that the samples collected from

Pollachi main road (site number 2) are having maximum extinction co-efficient of 57.75. This site is taken as reference to have maximum quartz. The site number 3 (Town bus stand) is having minimum extinction co-efficient of 25.79. With these two limits, the other sites may be arranged.

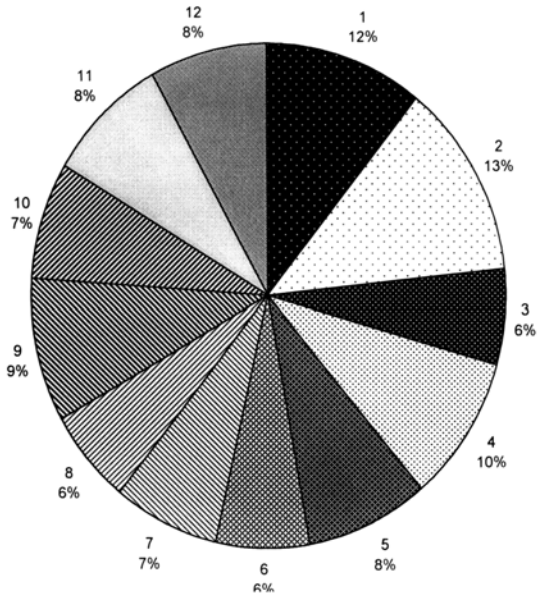

Figure 3. Extinction co-efficient of quartz for all the sites

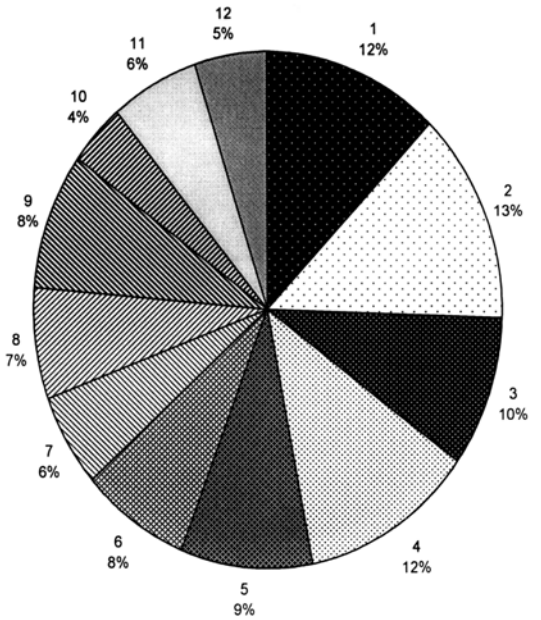

Figure 4. Extinction co-efficient of kaolinite for all the sites.

Kaolinite : The characteristic peak chosen for the determination of extinction co-efficient for the kaolinite is 3690 cm^{-1}. From Figure 4, it is observed that the samples collected from Pollachi main road (site number 2) are having maximum extinction co-efficient of 63.73. This site is taken as reference to have maximum kaolinite. This site number 10 (Ukkadam) is having minimum extinction co-efficient of 18.32.

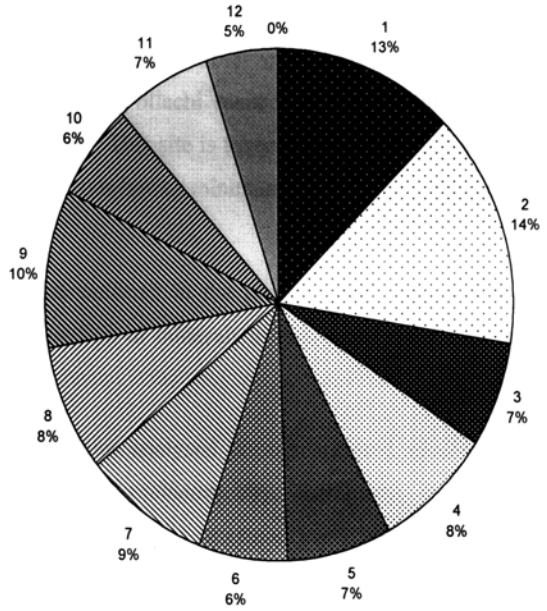

Figure 5. Extinction co-efficient of asbestos for all the sites

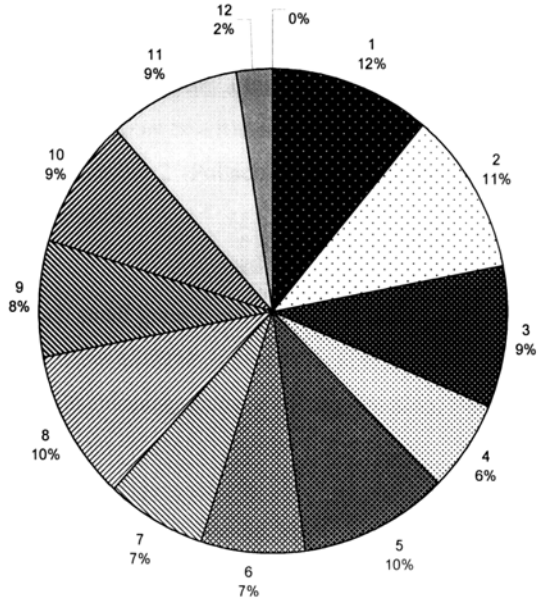

Figure 6. Extinction co-efficient of calcite for all the sites.

Asbestos : The characteristic peak chosen for the determination of extinction co-efficient for the asbestos is 1033 cm^{-1}. From Figure 5, it is observed that the samples collected from Pollachi main road (site number 2) are having maximum co-efficient of 147.32. This site is taken as reference to have maximum asbestos. The site number 12 (Kalveerampalayam) is having minimum extinction co-efficient of 49.76.

Catcite : The characteristic peak chosen for the determination of extinction co-efficient for the calcite is 1424 cm^{-1}. From Figure 6, it is observed that the samples collected from Mofussul bus stand (site number 1) and Pollachi main road (site number 2) are having maximum extinction co-efficient of 82.50. This site is taken as reference to have maximum Calcite. The site number 12 (Kalveerampalayam) is having minimum extinction co-efficient of 18.30.

4. Conclusion

The improved technique outlined in the present paper provides a rapid, reproducible and accurate method of determination of minerals in dust qualitatively. From the above studies it is concluded as follows.

1. The various dust samples analysed through infrared spectroscopic technique, collected from different sites of Coimbatore city, Tamilnadu, indicates the presence of quartz, asbestos, kaolinite, calcite, hematite, montmorillonite, nacrite and coal.
2. Among these different minerals, with reference to the appearance of number of peaks, quartz, calcite, asbestos and kaolinite are consider to be main (or) major constituent of the dust samples. Hematite and coal are considered to be minor minerals. The minerals such as montmorillonite and nacrite are considered to be associate minerals which may be found in traces.
3. The availability of quartz, kaolinite, asbestos, and calcite among the various sites were determined through extinction co-efficient of all these samples. From these overall observations, the site number 2 (Pollachi Main Road) are having maximum hazardous minerals than the other sites.
4. The inhalation of such small sized disordered minerals can create lung diseases. The toxicity of these minerals is proportional to the concentration. These forms of disease are progressive with a continuing decrease of lung function, even in the absence of further dust exposure.

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